S-XRF and Atmospheric Aerosols: Health, Visibility, and Climate Change

Thomas A. Cahill,[1] Steven S. Cliff,[1] Kevin D. Perry,[1] Michael Jimenez-Cruz,[1] Peter B. Kelly,[1] James Shackelford,[1] Scott A. McHugo,[2] Al Thompson[2]

[1]DELTA Group, Departments of Applied Science, Atmospheric Sciences, Chemistry, Physics, and Chemical Engineering/Materials Science, University of California Davis 95616

[2]Center for X-Ray Optics, ALS, Lawrence Berkeley National Laboratory 94270

INTRODUCTION

Great technical progress was made on Beam Line 10.3.1 in 2000 leading to a final configuration for sample handling, vacuum analysis, beam spot, beam energy, and computer reduction codes. The synchrotron- X-ray Fluorescence (S-XRF) with the white (4 keV - 18 keV) beam gives enough flux to achieve optimum count rates in the Si(Li) detector for even thin aerosol samples in vacuum for elements sodium and heavier. An automatic sample changer was designed and built at UC Davis to sit behind the focal plane in a non-interfering position, allowing control by LBNL computers on a micron resolution and making set up and take down far easier. The vacuum system allowed pressures of about 9 torr, more than adequate to reduce the argon peak and eliminate the background from air, immediately raising the sensitivities by a factor of roughly 20 and extending the elemental range down to sodium. Equally important, we were able to install the internationally accepted x-ray analysis code AXIL, calibrate (with 50 thin film standards) the x-ray yield, and transfer data into an Excel spread sheet. These changes have now made the system far more user friendly.

As shown below for iron, other elements are similar or better, the documented sensitivities are roughly 1,000 better than the brand new US Environmental Protection Agency's (EPA) National Speciating Aerosol Network. Note that the US EPA and IMPROVE methods took 15 minutes of analysis time with sample collection time of 24 hours, while the S-XRF sensitivities are in 1 minute analysis time and for a sample collection time of only 4 hrs. The gains are achieved by both high S-XRF sensitivity and by matching sample collection and beam analysis areas. The values are minimum detectable limits in picograms of iron per cubic meter of air sampled.

US EPA XRF Air Filters 24 hours	UCD IMPROVE PIXE/XRF Air Filters 24 hours	DELTA UCD/ALS S-XRF Air Filters 24 hours	DELTA UCD/ALS S-XRF Slot Impactor 4 hours	DELTA UCD/ALS S-XRF Jet Impactor 4 hours
560 pg/m^3	70 pg/m^3	26 pg/m^3	15 pg/m^3	0.6 pg/m^3

These advances were partially offset by the regrettable loss of Dr. Scott McHugo to industry.

APPLICATIONS

The first major test of the system was in the cross boundary Mexico-Texas study called BRAVO. The key question addressed by the ALS was the ability to see trace metals on an hourly basis for 4 continuous months in 1999. With trajectory analysis, this allows a single site to monitor fine particles and haze throughout the entire period. When a haze episode occurs, then additional sizes (up to 8) can be analyzed to identify exactly those sources associated with the haze. These samples were analyzed in air, since in spring the vacuum system had not been established. Thus, we have succeeded in shortening the time increment for collection of an aerosols sample from ambient air at a clean sites (down to 30 minutes if necessary) and measuring trace elements (to 0.1 ng/m^3) by using synchrotron x-ray fluorescence (SXRF) microprobe on beam line 10.3.1, with analysis times of about 1 minute. The first phase involved almost 3,000 individual analyses, and the next phase almost 1,500. The early results showed the ability top cleanly separate all major pollution sources in Texas and Mexico, notably the city of Monterrey, the Carbon II coal fired power plants, biomass smoke from central and southern Mexico, the petrochemical industry of Texas, and even coal fired power plants in the southeastern USA.

The first major test of the vacuum system resulted in greatly improved sensitivities and the ability to quantitatively measure elements as light as sodium. Our experiments were in preparation for the large ACE-Asia study in Spring 2001, which will now be depending heavily on S-XRF for elemental analysis. This study spans almost 120^o of longitude, from Dunhuang in western China to Crater Lake, Oregon and Poker Flat, Alaska to Hawaii. We are employing our rotating drum impactors that separate aerosols into either 3 or 8 size modes, with temporal resolutions ranging from 30 minute to 4 hours over 6-week period. The test in Kyoto, December 1999, used the 3-DRUM impactor. Data for major elements and trace elements are shown below for the key optically efficient size mode 1.15 > Dp > 0.34 microns.

The sensitivity achieved for the trace elements was roughly 0.1 ng/m^3, or roughly that achieved in a 24 filter sample in the IMPROVE network, until now, the optimum achieved in routine practice. Each S-XRF analysis was roughly 1 minute long.

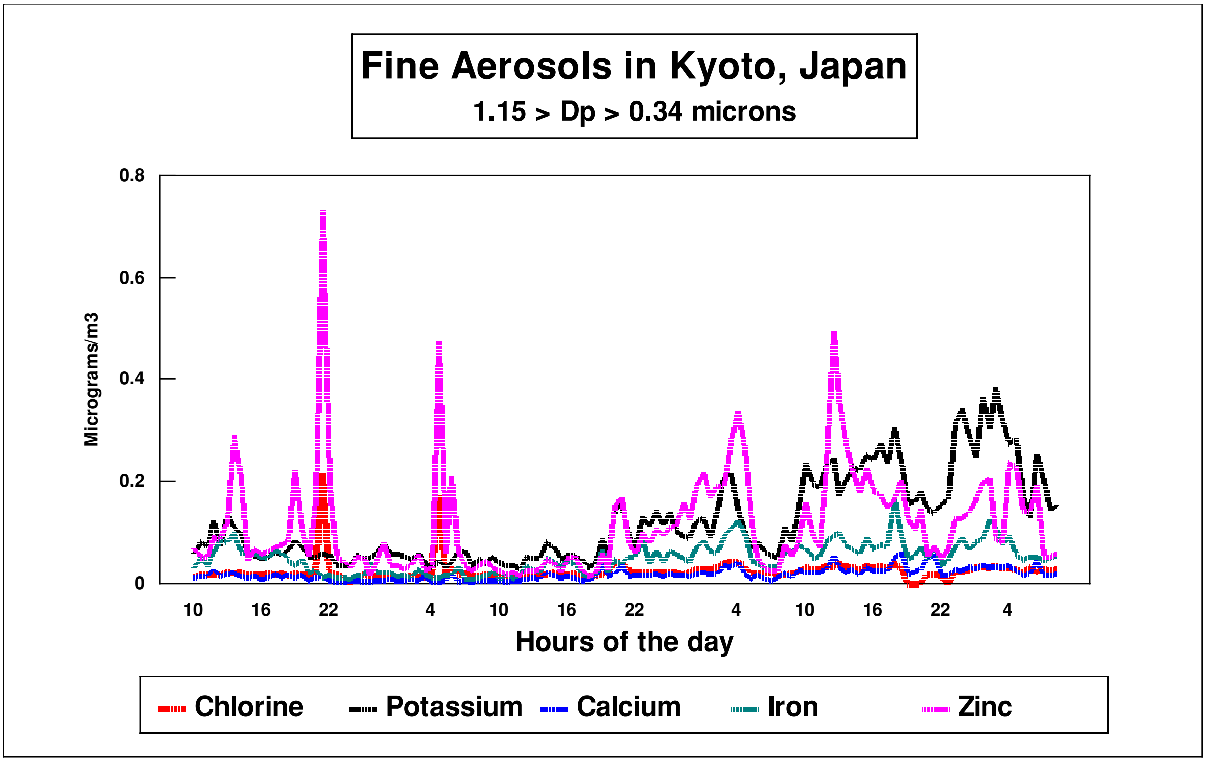
The results were startling in that they were qualitatively different than expected, based on earlier data from 24 duration filter samples. In particular, the mass levels on the first two days were caused by two sharp spikes, each no more than 30 minutes long, while the mass on the second half was caused by persistent aerosols of lower concentration.

A second major use of the ALS was in the Fresno (CA) Asthmatic Children Environmental Study (FACES). This study is designed to associate environmental impacts with asthma attacks in children. Since these tend to occur in a period of a few hours, the program was faced with the daunting task of establishing size and composition roughly hourly, which is simply not possible with traditional methods. The same system as used as for Kyoto, but with 6-hour time resolution and 8 size modes, not 30-minute resolution and 3 size modes. One of the first results showed a great deal of variability in the sub-micron modes, as each source appears to have a rather limited and characteristic size distribution. This is actually good news, as it allows much greater specificity in establishing sources. The second is that the very black samples included a great deal of ultra-fine diesel aerosol. Normally, fine potassium is associated with biomass smoke, until now, thought to be the major source in fall in Fresno. The fact that diesel exhaust is a far greater source helps direct mitigation into efficient channels.

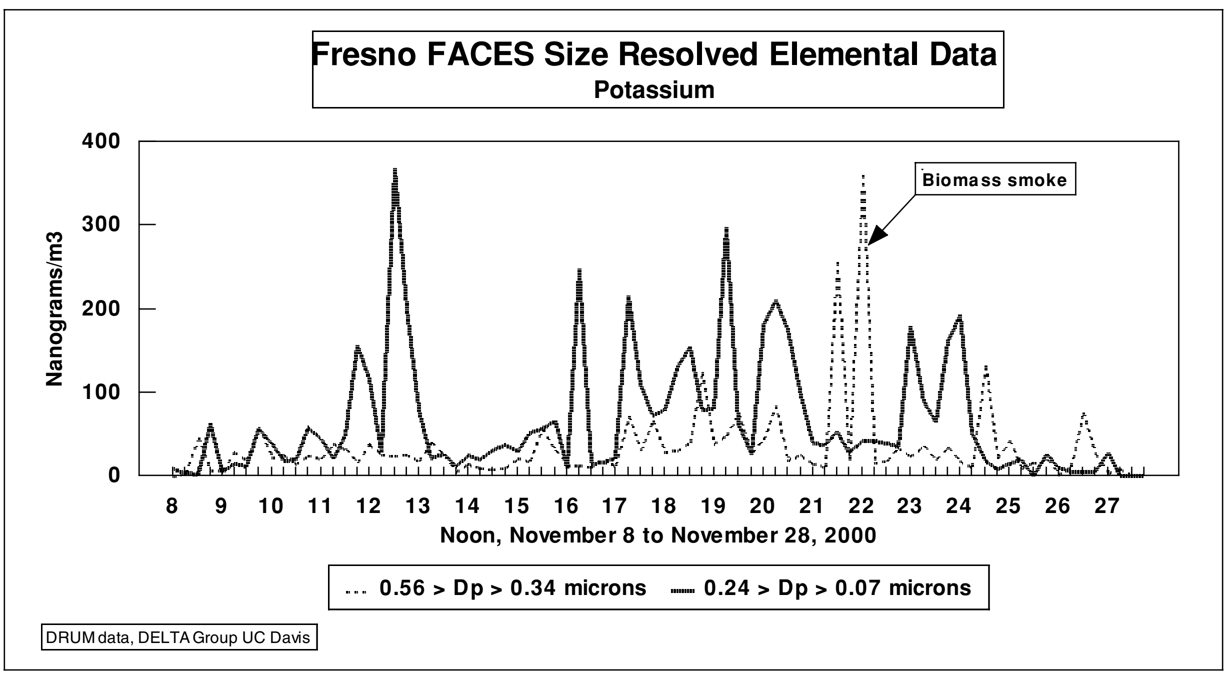
Other major programs included a joint US DOE/Texas Natural Resources Commission study of the air of Houston, Texas, analysis of ultra-fine aerosols from "clean diesel" technology, and a major study of the climatic impact of trans-Atlantic Saharan /Sahel dust in Puerto Rico.

This work was supported by NSF/Atmospheric Chemistry, United States Navy, United States National Park Service (US NPS), United States Environmental Protection Agency (US EPA), California Air Resources Board (CA ARB), University of California-Pacific Rim.

Principal Investigator: Thomas A. Cahill, DELTA Group, Departments of Applied Science, Atmospheric Sciences, Chemistry, Physics, and Chemical Engineering/Materials Science, University of California Davis. Email: tacahill@ucdavis.edu. Telephone: (530) 752-1120. World Wide Web: http://delta.ucdavis.edu.



Fine Aerosols in Kyoto, Japan
1.15 > Dp > 0.34 microns
Micrograms/m3
0.8
0.6
0.4
0.2
0
10
16
22
4
10
16
22
4
10
16
22
4
Hours of the day
Chlorine
Potassium
Calcium
Iron
Zinc



Fresno FACES Size Resolved Elemental Data
Potassium
Nanograms/m3
400
300
200
100
0
Biomass smoke
8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27
Noon, November 8 to November 28, 2000
0.56 > Dp > 0.34 microns
0.24 > Dp > 0.07 microns
DRUM data, DELTA Group UC Davis